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# Fitted Electronic Density Functions from H to Rn for Use in Quantum Similarity Measures: *cis*-Diammine-Dichloroplatinum(II) Complex as an Application Example

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*Received 7 December 1998; accepted 28 January 1999*

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**ABSTRACT:** A consistent set of fitted electronic density functions was generated for the elements from hydrogen to radon using an algorithm based on the elementary Jacobi rotations (EJR) technique. The main distinguishing attribute of this fitting procedure is the production of approximated electronic density functions with positive definite expansion coefficients; in this way, the statistical meaning of the probability distribution is preserved. The methodology, which was fully described previously, was modified in this work to improve and accelerate the fitting procedure. This variation concerns the optimization method employed to obtain the optimal angle of the EJR, implementing an algorithm based on a Taylor series expansion. Additionally, a new *1S-Type* Gaussian basis set for atoms H to Rn is presented, that was fitted from a primitive basis set of Huzinaga. Fitted density functions facilitate theoretical calculations over large molecules and may be employed in many areas of computational chemistry, for example, in quantum similarity measures (QSM). To verify the basis set, a sound example related to QSM applications is given. This corresponds to the comparison of experimental structures obtained from X-ray determination for *cis*-diamminedichloroplatinum(II) complex with

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Contract/grant sponsor: CICYT; contract/grant number: SAF 96-0158

Contract/grant sponsor: Fundació Maria Francisca de Roviralta

Contract/grant sponsor: EC; contract/grant number: ENV4-CT97-0508

optimized molecular geometries using several theoretical methods to quantify the differences between the analyzed levels of theory. © 1999 John Wiley & Sons, Inc. J Comput Chem 20: 911–920, 1999

**Keywords:** elementary Jacobi rotations (EJR); atomic shell approximation (ASA); quantum similarity measures (QSM); *cis*-diamminedichloroplatinum; promolecular density functions

## Introduction

Nowadays, precise theoretical *ab initio* studies of large molecular systems or transition metal complexes are usually limited by the number and kind of atoms involved, which is due to the fact that computational requirements clearly increase with the number of basis functions. The main *ab initio* calculation hindrance is generally located in the computation of the cumbersome four-center integrals. These integrals, which appear in the calculation of two-electron repulsion energies, as well as in quantum similarity measures (QSM),<sup>1–5</sup> can be readily evaluated if approximated electronic density functions are used instead of *ab initio*. These simplified electron density clouds, commonly constructed as linear combinations of Gaussian-type functions, are generally obtained from a fitting procedure consisting of optimizing the coefficients of the linear expansion by minimizing the quadratic error integral between *ab initio* and the approximated function. In the literature one can find different fitting algorithms<sup>6–11</sup> for first-order electronic density functions,  $\rho(\mathbf{r})$ , but not all of them take into account the conditions needed to obtain a definite positive  $\rho(\mathbf{r})$ . Recently, the atomic shell approximation (ASA)<sup>10,11</sup> was described, consisting of a linear expansion of 1S GTO functions to the  $\rho(\mathbf{r})$ , where a set of convex conditions are imposed to the expansion coefficients, yielding a fitted density function with the suitable features of a probability distribution.

In a previous article<sup>11</sup> the atomic density fitting of the 3-21G basis set for atoms H to Kr was examined in complete detail using a robust algorithm based on the elementary Jacobi rotation (EJR) technique.<sup>12</sup> This first work demonstrated that an EJR algorithm based on norm conserving orthogonal transformations provides an accurate method for obtaining fitted atomic density functions with the additional attribute that the expansion coefficients remain positive definite within the proce-

dure. Furthermore, in subsequent studies the usefulness of the fitted basis set to be applied in QSM<sup>13–18</sup> was confirmed, employing a *promolecular* method to construct the molecular electronic density functions. To further improve the atomic basis set fitting and permit QSM calculations over large atoms, a Huzinaga atomic basis set available for atoms H to Rn<sup>19,20</sup> was considered in the present study. On the basis of the fitting procedure put forward in the previous work,<sup>11</sup> where a general methodology was established, minimal modifications, involving the use of Taylor series expansions, were implemented in the program to improve the efficiency of the search for the optimal EJR rotation angle.

## ASA FIRST-ORDER DENSITY FUNCTIONS

Accurate analytical representations of electron densities are obtained using the LCAO-MO approximation, corresponding to the expression

$$\rho_A(\mathbf{r}) = \sum_{\mu, \nu \in A} D_{\mu\nu} \chi_{\mu}^*(\mathbf{r}) \chi_{\nu}(\mathbf{r}), \quad (1)$$

where  $\{D_{\mu\nu}\}$  are the elements of the charge-bond order matrix and  $\{\chi_{\mu}\}$  is the atomic orbital basis set. To reduce computational requirements, simplified density functions have been proposed.<sup>6–11</sup> One of these is ASA electron density,<sup>10,11</sup> which is constructed by means of a linear combination of spherical Gaussian functions

$$\rho_A^{\text{ASA}}(\mathbf{r}) = \sum_{i \in A} w_i |\varphi_i(\mathbf{r})|^2, \quad (2)$$

where  $\{w_i\}$  represents the ASA coefficients and  $\{\varphi_i\}$  denotes the set of the corresponding 1S-type functions. Considering electron density as a probability distribution which may be definite positive *everywhere*, ASA coefficients of the linear expansion (2) have to be positive to preserve the statistical meaning of the density function.<sup>21</sup> Within this context, a set of convex conditions is imposed on the  $\{w_i\}$

coefficients, corresponding to

$$\left\{ w_i \in R^+ \quad \forall i \quad \wedge \quad \sum_{i \in A} w_i = 1 \right\}, \quad (3)$$

which provides a normalized description of the electron density:

$$\int \rho_A^{\text{ASA}}(\mathbf{r}) d\mathbf{r} = 1.$$

Furthermore, a *promolecular* approximation can be used in order to avoid the computation of *ab initio* molecular density functions, consisting of building the molecular electronic distribution as a sum of individual atomic densities.<sup>11,13–18</sup>

## FITTING ALGORITHM

In a recent article<sup>11</sup> a broad description of ASA fitting was carried out, giving exhaustive details of the whole procedure. Fundamentally the method is based on two parts: generation of ASA exponents using *even-tempered* geometric sequences<sup>22</sup> and optimization of coefficients and exponents using an EJR technique and a Newton method, respectively. Here, on the basis of the established general procedure,<sup>11</sup> only some parts of the algorithm will be attended to, corresponding to some improvements made on the optimization procedure of ASA coefficients. Basically, the optimal ASA coefficients are obtained minimizing the quadratic error integral function between *ab initio* and ASA electronic density functions:

$$\varepsilon^{(2)} = \int |\rho_A(\mathbf{r}) - \rho_A^{\text{ASA}}(\mathbf{r})|^2 d\mathbf{r}, \quad (4)$$

subjected to the constraints described in eq. (3). Substituting the density functions  $\rho_A(\mathbf{r})$  and  $\rho_A^{\text{ASA}}(\mathbf{r})$  with the expressions (1) and (2), respectively, and developing the square term appearing in eq. (4), a simple matrix notation of the function  $\varepsilon^{(2)}$  can be obtained:

$$\varepsilon^{(2)} = Z_{\text{AA}} + \mathbf{w}^\top \mathbf{Z} \mathbf{w} - 2\mathbf{b}^\top \mathbf{w}, \quad (5)$$

where  $Z_{\text{AA}}$  denotes an *ab initio* overlaplike quantum self-similarity measure (QS-SM),<sup>1–5</sup> defined by the integral

$$\begin{aligned} Z_{\text{AA}} &= \int \rho_A(\mathbf{r}) \rho_A(\mathbf{r}) d\mathbf{r} \\ &= \sum_{\mu, \nu \in A} D_{\mu\nu} \sum_{\lambda, \sigma \in A} D_{\lambda\sigma} \int \chi_\mu^*(\mathbf{r}) \chi_\nu(\mathbf{r}) \\ &\quad \times \chi_\lambda^*(\mathbf{r}) \chi_\sigma(\mathbf{r}) d\mathbf{r}, \end{aligned} \quad (6)$$

whereas the vector  $\mathbf{w} = \{w_i\}$  contains the set of ASA coefficients, the matrix  $\mathbf{Z} = \{Z_{ij}\}$  corresponds to the ASA similarity measures between the atomic shells  $i$  and  $j$ ,

$$Z_{ij} = \int |\varphi_i(\mathbf{r})|^2 |\varphi_j(\mathbf{r})|^2 d\mathbf{r}, \quad (7)$$

and the elements of the vector  $\mathbf{b} = \{b_i\}$  involve the integrals between *ab initio* density function and each  $i$ th ASA function

$$b_i = \int |\varphi_i(\mathbf{r})|^2 \rho_A(\mathbf{r}) d\mathbf{r}. \quad (8)$$

The set of positive definite real coefficients  $\{w_i\}$  can be substituted by a complex coefficient set,  $\mathbf{x} = \{x_i\}$ , defined as  $w_i = |x_i|^2$ . In this way, the first restriction described in eq. (3) is fulfilled, and the function  $\varepsilon^{(2)}$  is transformed to the expression

$$\varepsilon^{(2)} = Z_{\text{AA}} + \sum_{i,j \in A} x_i^2 x_j^2 Z_{ij} - 2 \sum_{i \in A} x_i^2 b_i. \quad (9)$$

An elegant method for optimizing the coefficients  $\{x_i\}$  is provided by the EJR technique. This approach, initially developed as a diagonalization method for symmetric matrices,<sup>12</sup> is based on norm conserving orthogonal transformations. This quality is particularly advantageous because, if the initial set of coefficients fulfill the normalization condition given in eq. (3),  $\sum |x_i|^2 = 1$ , then this constraint is conserved throughout all the procedure. The application of an EJR transformation,  $\mathbf{J}_{pq}(\alpha)$ , over the vector  $\mathbf{x}$  can be described by the equations

$$\begin{aligned} \dot{x}_p &\leftarrow cx_p - sx_q \\ \dot{x}_q &\leftarrow sx_p + cx_q, \end{aligned} \quad (10)$$

where only the elements  $p$  and  $q$  are modified. The symbols  $c$  and  $s$  appearing in eq. (10) determine the cosine and sine of the rotation angle  $\alpha$ . In order to compute the variation of the function  $\varepsilon^{(2)}$  with respect to the active pair of elements  $\{x_p, x_q\}$ , first it is necessary to isolate these elements from the rest in eq. (9), and then apply the EJR  $\mathbf{J}_{pq}(\alpha)$  over this equation, yielding

$$\begin{aligned} \delta \varepsilon^{(2)} &= \delta x_p^4 Z_{pp} + \delta x_q^4 Z_{qq} \\ &\quad + 2\delta(x_p^2 x_q^2) Z_{pq} + 2\delta x_p^2 \sum_{i \neq p, q} x_i^2 Z_{pi} \\ &\quad + 2\delta x_q^2 \sum_{i \neq p, q} x_i^2 Z_{iq} \\ &\quad - 2b_p \delta x_p^2 - 2b_q \delta x_q^2. \end{aligned} \quad (11)$$

The parameters  $\delta x_p^2$ ,  $\delta x_q^2$ ,  $\delta x_p^4$ ,  $\delta x_q^4$ , and  $\delta(x_p^2 x_q^2)$  are easily calculated (see ref. 11), giving as a result a quartic equation with respect to  $s$  and  $c$ :

$$\delta \mathcal{E}^{(2)} = E_{04}s^4 + E_{13}cs^3 + E_{02}s^2 + E_{11}cs. \quad (12)$$

The optimal sine,  $s^*$ , related to the EJR procedure is obtained by imposing a zero gradient condition to the function  $\delta \mathcal{E}^{(2)}$ :  $d\delta \mathcal{E}^{(2)}/ds = 0$ . As described in the first article of this series,<sup>11</sup> the optimal EJR angle,  $\alpha^*$ , is obtained by solving the resulting second-degree equation by means of an iterative algorithm. The aim of the present work is to improve the procedure for calculating  $\alpha^*$ . In this way, some modifications have been introduced in the algorithm, consisting in replacing the sine and cosine expressions of eq. (10) by a Taylor series expansion,<sup>23</sup> as may be done in parent SCF procedures<sup>24</sup>:

$$\begin{aligned} c &= \cos(\alpha) = 1 - \frac{1}{2}\alpha^2 + \theta(\alpha^3) \\ s &= \sin(\alpha) = \alpha \left(1 - \frac{1}{6}\alpha^2\right) + \theta(\alpha^4). \end{aligned} \quad (13)$$

From this reduced notation of the sine and cosine it is possible to define the subsequent product of variables up to third-order on  $\alpha$ :

$$\begin{aligned} s^2 &\approx \alpha^2 \\ s^3 &\approx \alpha^3 \\ s^4 &\approx 0 \\ cs &\approx \alpha \left(1 - \frac{2}{3}\alpha^2\right) \\ cs^3 &\approx \alpha^3. \end{aligned} \quad (14)$$

Consequently, by substituting these variables into eq. (12) a simpler expression is obtained:

$$\delta \mathcal{E}^{(2)} = \alpha^3 a + \alpha^2 b + \alpha c, \quad (15)$$

where  $a = E_{13} - (2E_{11}/3)$ ,  $b = E_{02}$ , and  $c = E_{11}$ . When a stationary point condition is taken on (15), the following equation is obtained:

$$\frac{d\delta \mathcal{E}^{(2)}}{d\alpha} = 3\alpha^2 a + 2\alpha b + c = 0 \quad (16)$$

and the second derivative determines the minimum condition

$$\frac{d^2\delta \mathcal{E}^{(2)}}{d\alpha^2} = 6\alpha a + 2b. \quad (17)$$

The optimal angle is then

$$\alpha^* = \alpha_+ = \frac{1}{3a} \left[ -b + (b^2 - 3ac)^{1/2} \right], \quad (18)$$

so the optimal cosine and sine are given by

$$\begin{aligned} c^* &\approx 1 - \frac{1}{2}\alpha_+^2 \\ s^* &\approx \alpha_+ \left(1 - \frac{1}{6}\alpha_+^2\right). \end{aligned} \quad (19)$$

Substituting eq. (19) in eq. (10), a simple expression for the coefficient set variation is obtained:

$$\begin{aligned} \dot{x}_p &\leftarrow c^* x_p - s^* x_q \\ &= x_p - \alpha_+ x_q + \frac{1}{2}\alpha_+^2 \left( -x_p + \frac{1}{3}\alpha_+ x_q \right) \\ \dot{x}_q &\leftarrow s^* x_p + c^* x_q \\ &= \alpha_+ x_p + x_q - \frac{1}{2}\alpha_+^2 \left( \frac{1}{3}\alpha_+ x_p + x_q \right), \end{aligned} \quad (20)$$

which gives the optimal EJR transformation. Evidently, the main advantage of the approach presented here is the replacement of an iterative method by a simpler determination of  $\alpha^*$ . This will provide a faster algorithm.

## ATOMIC ASA DENSITY FITTING OF AB INITIO HUZINAGA BASIS SET

As an application example of the EJR algorithm new development, an atomic basis set was fitted for atoms H to Rn. *Ab initio* calculations for the fitting procedure were obtained from a Huzinaga basis set<sup>19,20</sup> using the ATOMIC program. Among the multiple basis set schemes provided by refs. 19 and 20, the set of primitive functions listed in Table I was chosen, which is described using the original Huzinaga's contraction scheme notation. The fitting process was performed using the GATOMIC program,<sup>26</sup> which includes the modifications on the EJR algorithm described in the previous section. First a minimal ASA basis set for the atoms H to Rn was calculated, corresponding to the least number of fitted functions needed to obtain a value of the function  $\mathcal{E}^{(2)}$  inferior to 0.01 au. In a similar way, as in the previous study for the 3-21G basis set,<sup>11</sup> the number of atomic shells per atom varies with respect to the row of the periodic table from two functions for H and He atoms to seven functions for the elements of the sixth row. Recent studies demonstrated that this

**TABLE I.**  
**Notation for Contracted Gaussian Primitive Basis Set.**

Atomic Symbol	Huzinaga Notation <sup>a</sup>
H, He	3
Li, Be	33
B, C, N, O, F, Ne	33 / 3
Na, Mg	432 / 3
Al, Si, P, S, Cl, Ar	432 / 42
K, Ca	4322 / 42
Sc, Ti, V, Cr, Mn, Fe, Co,	4322 / 42 / 3
Ni, Cu, Zn	
Ga, Ge, As, Se, Br, Kr	4322 / 422 / 3
Rb, Sr	43222 / 422 / 3
Y, Zr, Nb, Mo, Tc, Ru, Rh,	43222 / 422 / 33
Pd, Ag, Cd	
In, Sn, Sb, Te, I, Xe	43222 / 4222 / 42
Cs, Ba	432222 / 4222 / 42
La	432222 / 4222 / 42 / 3
Ce, Pr, Nd, Pm, Sm, Eu, Gd,	432222 / 4222 / 42 / 4
Tb, Dy, Ho, Er, Tm, Yb	
Lu, Hf, Ta, W, Re, Os, Ir,	432222 / 4222 / 423 / 3
Pt, Au, Hg	
Tl, Pb, Bi, Po, At, Rn	432222 / 42222 / 422 / 3

<sup>a</sup>The expansion pattern ( $K_{s1}, K_{s2}, \dots / K_{p1}, K_{p2}, \dots / K_{d1}, K_{d2}, \dots / K_{f1}, \dots$ ) is used as the notation to specify the number of terms in the expansion of the atomic basis set.

minimal atomic basis set is sufficient to obtain excellent results for QSM applications.<sup>13–18</sup> The main results for the ASA fitting are presented in Table II, where the values for the Hartree–Fock (HF) energy, normalized *ab initio* QS-SM, number of fitted functions, quadratic error integral function, and relative error produced in the QS-SM for the atoms H to Rn are summarized. In the last column of Table II the percent error in  $Z_{AA}$  evaluation is given. Because the procedure optimizes  $\varepsilon^{(2)}$  rather than  $Z_{AA}$  values, the self-similarity errors are sufficiently low and vary in a random manner. Coefficients and exponents for this basis set of ASA functions are available for downloading at a worldwide web site.<sup>27</sup>

In addition to the minimal basis set for atoms H to Rn, a detailed study was performed for several atoms to verify the correctness of the ASA fitting methodology. Table III shows the most significant parameters related to the ASA fitting for H, C, O, N, F, P, S, and Cl atoms, employing from two to eight functions. The analyzed parameters are the values of the function  $\varepsilon^{(2)}$  and the relative error performed in the calculation of ASA QS-SM and normalized one-electron potential energy,  $V(\mathbf{r})$ ,

which may be defined as

$$V(\mathbf{r}) = - \int \frac{\rho_A^{\text{ASA}}(\mathbf{r})}{|\mathbf{r}|} d\mathbf{r} = - \sum_{i \in A} w_i \int \frac{1}{|\mathbf{r}|} |S_i(\mathbf{r})|^2 d\mathbf{r}. \quad (21)$$

As the number of ASA functions increases, the quadratic error integral function quickly decreases. Moreover, from Table III it is possible to appreciate a relationship between the relative error produced in  $Z_{AA}$  and  $V(\mathbf{r})$  values, giving similar variations. There is a general tendency to decrease the value of both parameters when the number of ASA functions increases, but not as pronounced as in the values of the  $\varepsilon^{(2)}$  function. In fact, the main conclusion that can be drawn from Table III is that with few ASA functions it is possible to obtain an excellent fit.

### QSM APPLICATION EXAMPLE

In many theoretical studies concerning geometry optimization and energy minimization, the selection of the appropriate methodology that is used becomes an initial and essential process, which, in many cases, is not taken into account. It is crucial therefore to use suitable 3-dimensional (3-D) structures in the majority of computational chemistry calculations, for example, in the study of path reaction, where small changes on the molecular geometry can provide incorrect conclusions and results. A method for quantitatively comparing calculated molecular geometries obtained from different approaches and levels of theory can be based on QSM, as has been demonstrated in a recent work,<sup>14</sup> which relies on determining the differences between experimental and theoretical structures. In this work, the *cis*-diammine-dichloroplatinum(II) complex (*cis*-DDP), an anti-cancer drug,<sup>28</sup> was chosen to provide an application example. This transition metal complex is a good test for the application of the fitted atomic Gaussian basis set presented in the previous section, because in it a heavy atom, such as Pt, takes part. First a search of the Cambridge Structural Database (CDS)<sup>29</sup> was performed, and two X-ray crystallographic structures for the *cis*-DDP complex were found: *cis*-DDP dimethylformamide solvate (CUKRAB) and 18-Crown-6 bis(dimethylacetamide) bis(*cis*-DDP) (CUSRAJ).

Eight different structures are compared, two of them from X-ray analysis and six from theoretical calculations. These last geometries were fully opti-

TABLE II.   
Fitting Results for *Ab Initio* Huzinaga Atomic Basis Set for Atoms H to Rn: Minimal ASA Basis Set.

Atomic Symbol	Electronic State	HF <sup>a</sup>	Z <sub>AA</sub>	n <sup>b</sup>	ε <sup>(2)</sup>	Z <sub>AA</sub> Error (%)
H	<sup>2</sup> S	−4.969792526E-01	0.03939	2	0.0001463	−2.5725
He	<sup>1</sup> S	−2.835679876E+00	0.18800	2	0.0010896	−3.1134
Li	<sup>2</sup> S	−7.378092307E+00	0.34452	3	0.0007891	0.0486
Be	<sup>1</sup> S	−1.447611084E+01	0.51917	3	0.0009877	0.0430
B	<sup>2</sup> P	−2.437272923E+01	0.69367	3	0.0012675	−0.0120
C	<sup>3</sup> P	−3.745282379E+01	0.87234	3	0.0015070	−0.1105
N	<sup>4</sup> S	−5.406244335E+01	1.06079	3	0.0020636	−0.2125
O	<sup>3</sup> P	−7.433921998E+01	1.25522	3	0.0026446	−0.3606
F	<sup>2</sup> P	−9.877655073E+01	1.46136	3	0.0036004	−0.5171
Ne	<sup>1</sup> S	−1.277187909E+02	1.67697	3	0.0046583	−0.6919
Na	<sup>2</sup> S	−1.614200178E+02	1.91971	4	0.00392992	−1.1778
Mg	<sup>1</sup> S	−1.991000990E+02	2.15931	4	0.0045979	0.0805
Al	<sup>2</sup> P	−2.415557168E+02	2.41336	4	0.0046660	0.1245
Si	<sup>3</sup> P	−2.884848502E+02	2.66285	4	0.0048889	0.1386
P	<sup>4</sup> S	−3.402953458E+02	2.91708	4	0.0050630	0.1379
S	<sup>3</sup> P	−3.970195424E+02	3.17561	4	0.0052278	0.1315
Cl	<sup>2</sup> P	−4.589288466E+02	3.43832	4	0.0053933	0.1248
Ar	<sup>1</sup> S	−5.261904122E+02	3.70604	4	0.0055419	0.1181
K	<sup>2</sup> S	−5.984734792E+02	3.98451	5	0.0003748	−0.0376
Ca	<sup>1</sup> S	−6.760028693E+02	4.26335	5	0.0005072	−0.0848
Sc	<sup>2</sup> D	−7.588683361E+02	4.53727	5	0.0005682	−0.1017
Ti	<sup>3</sup> F	−8.474105511E+02	4.81189	5	0.0006353	−0.1103
V	<sup>4</sup> F	−9.417431646E+02	5.08829	5	0.0007111	−0.1282
Cr	<sup>5</sup> D	−1.042004521E+03	5.36746	5	0.0008079	−0.1432
Mn	<sup>6</sup> S	−1.148378100E+03	5.64709	5	0.0009094	−0.1577
Fe	<sup>5</sup> D	−1.260742127E+03	5.92997	5	0.0010303	−0.1695
Co	<sup>4</sup> F	−1.379478279E+03	6.21501	5	0.0011963	−0.1955
Ni	<sup>3</sup> F	−1.504675051E+03	6.50265	5	0.0013679	−0.2153
Cu	<sup>2</sup> D	−1.636468665E+03	6.79265	5	0.0015600	−0.2344
Zn	<sup>1</sup> S	−1.775056361E+03	7.08444	5	0.0017706	−0.2585
Ga	<sup>2</sup> P	−1.920361458E+03	7.38764	5	0.0024764	−0.3258
Ge	<sup>3</sup> P	−2.072336570E+03	7.69236	5	0.0034626	−0.4018
As	<sup>4</sup> S	−2.231077402E+03	8.00019	5	0.0047922	−0.4823
Se	<sup>3</sup> P	−2.396555652E+03	8.31116	5	0.0064939	−0.5650
Br	<sup>2</sup> P	−2.568968763E+03	8.62436	5	0.0086121	−0.6487
Kr	<sup>1</sup> S	−2.748411490E+03	8.94033	5	0.0093826	0.1030
Rb	<sup>2</sup> S	−2.934540749E+03	9.25956	6	0.0005184	0.0001
Sr	<sup>1</sup> S	−3.127572218E+03	9.58254	6	0.0006653	−0.0018
Y	<sup>2</sup> D	−3.327645322E+03	9.90583	6	0.0007058	−0.0025
Zr	<sup>3</sup> F	−3.534786249E+03	10.22872	6	0.0006814	−0.0045
Nb	<sup>6</sup> D	−3.749171741E+03	10.55127	6	0.0006842	−0.0013
Mo	<sup>7</sup> S	−3.970931775E+03	10.87764	6	0.0007322	−0.0011
Tc	<sup>6</sup> S	−4.200005584E+03	11.20902	6	0.0008185	−0.0043
Ru	<sup>5</sup> F	−4.436501714E+03	11.53459	6	0.0008571	−0.0013
Rh	<sup>4</sup> F	−4.680620905E+03	11.86623	6	0.0010686	−0.0015
Pd	<sup>3</sup> D	−4.932403048E+03	12.19779	6	0.0011365	−0.0017
Ag	<sup>2</sup> S	−5.191969936E+03	12.53153	6	0.0013018	−0.0011
Cd	<sup>1</sup> S	−5.459204578E+03	12.87027	6	0.0011572	−0.0064
In	<sup>2</sup> P	−5.735169884E+03	13.21283	6	0.0011237	−0.0143
Sn	<sup>3</sup> P	−6.017774127E+03	13.55495	6	0.0012129	−0.0237
Sb	<sup>4</sup> S	−6.308159013E+03	13.89854	6	0.0013923	−0.0310
Te	<sup>3</sup> P	−6.606280606E+03	14.24398	6	0.0015830	−0.0400

**TABLE II.**  
(Continued)

Atomic Symbol	Electronic State	HF <sup>a</sup>	Z <sub>AA</sub>	n <sup>b</sup>	$\varepsilon^{(2)}$	Z <sub>AA</sub> Error (%)
I	<sup>2</sup> P	−6.912293010E+03	14.59028	6	0.0018443	−0.0480
Xe	<sup>1</sup> S	−7.226259525E+03	14.94006	6	0.0021366	−0.0562
Cs	<sup>2</sup> S	−7.547866175E+03	15.29126	7	0.0016553	0.0108
Ba	<sup>1</sup> S	−7.877289281E+03	15.64351	7	0.0017217	0.0103
La	<sup>2</sup> F	−8.214448257E+03	15.98328	7	0.0016739	0.0095
Ce	<sup>3</sup> H	−8.560134394E+03	16.33152	7	0.0018155	0.0102
Pr	<sup>4</sup> I	−8.914118872E+03	16.67686	7	0.0018673	0.0103
Nd	<sup>5</sup> I	−9.276534340E+03	17.02378	7	0.0019810	0.0111
Pm	<sup>6</sup> H	−9.647454065E+03	17.37218	7	0.0019589	0.0102
Sm	<sup>7</sup> F	−1.002700168E+04	17.72103	7	0.0037966	−0.0997
Eu	<sup>8</sup> S	−1.041527457E+04	18.07250	7	0.0020845	0.0104
Gd	<sup>7</sup> F	−1.081201752E+04	18.42125	7	0.0027032	0.0136
Tb	<sup>6</sup> H	−1.121763004E+04	18.77186	7	0.0023948	0.0118
Dy	<sup>5</sup> I	−1.163216483E+04	19.12155	7	0.0024998	0.0121
Ho	<sup>4</sup> I	−1.205563774E+04	19.47228	7	0.0028697	0.0134
Er	<sup>3</sup> H	−1.248813204E+04	19.82825	7	0.0024286	0.0110
Tm	<sup>2</sup> F	−1.292976991E+04	20.17961	7	0.0025990	0.0115
Yb	<sup>1</sup> S	−1.338065566E+04	20.53538	7	0.0030558	0.0139
Lu	<sup>2</sup> D	−1.383819206E+04	20.89906	7	0.0058882	−0.1618
Hf	<sup>3</sup> F	−1.430740505E+04	21.26215	7	0.0029727	0.0121
Ta	<sup>4</sup> F	−1.478572471E+04	21.62753	7	0.0027151	0.0104
W	<sup>5</sup> D	−1.527318958E+04	21.99249	7	0.0031980	0.0128
Re	<sup>6</sup> S	−1.576990684E+04	22.35979	7	0.0030633	0.0120
Os	<sup>5</sup> D	−1.627572807E+04	22.73038	7	0.0032791	0.0128
Ir	<sup>4</sup> F	−1.679088555E+04	23.10037	7	0.0031468	0.0113
Pt	<sup>3</sup> F	−1.731541053E+04	23.46991	7	0.0033635	0.0125
Au	<sup>2</sup> D	−1.784934901E+04	23.84188	7	0.0034272	0.0122
Hg	<sup>1</sup> S	−1.839279390E+04	24.21301	7	0.0035502	0.0125
Tl	<sup>2</sup> P	−1.894511809E+04	24.58568	7	0.0037250	0.0120
Pb	<sup>3</sup> P	−1.950699432E+04	24.96366	7	0.0038512	0.0107
Bi	<sup>4</sup> S	−2.007825555E+04	25.34290	7	0.0039560	0.0094
Po	<sup>3</sup> P	−2.065884451E+04	25.72485	7	0.0041634	0.0091
At	<sup>2</sup> P	−2.124889325E+04	26.10476	7	0.0043268	0.0082
Rn	<sup>1</sup> S	−2.184844245E+04	26.48835	7	0.0045285	0.0080

<sup>a</sup>Hartree–Fock energy computed using the ATOMIC program.<sup>25</sup><sup>b</sup>Number of fitted atomic functions.

mized using the Gaussian 94 program<sup>30</sup> and LANL2DZ basis set, which includes relativistic effective core potential for the second and third row transition metals. The quantum chemical calculations were carried out at the HF level; second-, third-, and fourth-order Møller–Plesset (MP) approaches; and B3LYP level, which corresponds to a hybrid density functional theory (DFT). The main structural parameters for all molecular structures are presented in Table IV. Unfortunately, in both 3-D X-ray structures the *cis*-DDP complex is solvated. These environmental effects produce some minor deformations in the experimental geome-

tries of *cis*-DDP, providing a nonsymmetric and distorted 3-D structure, as can be observed in Table IV.

For the QSM computations,  $\rho_A^{\text{ASA}}(\mathbf{r})$  functions are constructed using a *promolecular* approximation<sup>13–18</sup> and the minimal basis set described in the previous section, employing three functions for N, four functions for Cl, and seven functions for Pt. Because X-ray analysis does not determine the position of hydrogen atoms, a possible alternative consists of comparing only the molecular fragment PtCl<sub>2</sub>N<sub>2</sub>. Molecular alignments were obtained using the MOLSIMIL program<sup>31</sup> and the methodol-

TABLE III. Fitting Results for *Ab Initio* Huzinaga Atomic Basis Set for Atoms H, C, N, O, F, P, S, and Cl.

		No. Fitted Atomic Functions						
		2	3	4	5	6	7	8
H	$\varepsilon^{(2)}$	$1.46 \times 10^{-4}$	$1.40 \times 10^{-6}$	$9.49 \times 10^{-7}$	$2.62 \times 10^{-7}$	$6.06 \times 10^{-8}$	$6.42 \times 10^{-9}$	$6.09 \times 10^{-9}$
	% $Z_{AA}$	-2.572	-0.006	0.123	0.018	0.013	0.006	0.004
	% $V(r)$	-0.950	-0.030	0.078	0.044	0.010	0.008	0.006
C	$\varepsilon^{(2)}$	$3.08 \times 10^{-2}$	$1.51 \times 10^{-3}$	$6.39 \times 10^{-5}$	$1.29 \times 10^{-5}$	$1.11 \times 10^{-5}$	$4.54 \times 10^{-6}$	$4.22 \times 10^{-6}$
	% $Z_{AA}$	2.455	-0.111	-0.107	0.008	0.006	0.008	0.005
	% $V(r)$	1.802	-0.347	-0.433	0.061	0.013	0.065	0.019
N	$\varepsilon^{(2)}$	$3.66 \times 10^{-2}$	$2.06 \times 10^{-3}$	$1.42 \times 10^{-4}$	$1.13 \times 10^{-5}$	$1.10 \times 10^{-5}$	$7.14 \times 10^{-6}$	$5.54 \times 10^{-6}$
	% $Z_{AA}$	2.246	-0.212	-0.191	-0.003	-0.003	0.014	0.011
	% $V(r)$	1.676	-0.502	-0.566	-0.002	0.017	0.085	0.071
O	$\varepsilon^{(2)}$	$4.26 \times 10^{-2}$	$2.64 \times 10^{-3}$	$2.98 \times 10^{-4}$	$2.15 \times 10^{-5}$	$1.39 \times 10^{-5}$	$7.26 \times 10^{-6}$	$6.31 \times 10^{-6}$
	% $Z_{AA}$	1.981	-0.361	-0.265	0.008	0.004	0.010	0.011
	% $V(r)$	1.419	-0.713	-0.708	0.047	0.007	0.037	0.054
F	$\varepsilon^{(2)}$	$4.90 \times 10^{-2}$	$3.60 \times 10^{-3}$	$5.27 \times 10^{-4}$	$2.39 \times 10^{-5}$	$1.60 \times 10^{-5}$	$7.42 \times 10^{-6}$	$7.34 \times 10^{-6}$
	% $Z_{AA}$	1.658	-0.517	-0.396	0.023	0.016	0.017	0.005
	% $V(r)$	1.172	-0.879	-0.870	0.132	0.058	0.066	0.025
P	$\varepsilon^{(2)}$	$1.35 \times 10^{-1}$	$4.37 \times 10^{-2}$	$5.06 \times 10^{-3}$	$4.57 \times 10^{-4}$	$7.87 \times 10^{-5}$	$1.16 \times 10^{-5}$	$1.02 \times 10^{-5}$
	% $Z_{AA}$	-2.462	-3.639	0.138	-0.015	-0.012	-0.006	-0.006
	% $V(r)$	-6.492	-7.827	0.113	-0.134	-0.103	-0.082	-0.063
S	$\varepsilon^{(2)}$	$1.63 \times 10^{-1}$	$6.02 \times 10^{-2}$	$5.23 \times 10^{-3}$	$4.17 \times 10^{-4}$	$1.32 \times 10^{-4}$	$2.00 \times 10^{-5}$	$1.17 \times 10^{-5}$
	% $Z_{AA}$	-3.023	-3.983	0.131	-0.011	-0.012	-0.006	-0.005
	% $V(r)$	-7.344	-8.507	0.141	-0.114	-0.137	-0.091	-0.081
Cl	$\varepsilon^{(2)}$	$1.94 \times 10^{-1}$	$7.83 \times 10^{-2}$	$5.39 \times 10^{-3}$	$3.72 \times 10^{-4}$	$6.18 \times 10^{-5}$	$2.30 \times 10^{-5}$	$1.94 \times 10^{-5}$
	% $Z_{AA}$	-3.451	2.056	0.125	-0.015	-0.015	-0.008	-0.006
	% $V(r)$	-7.974	1.118	0.143	-0.114	-0.111	-0.085	-0.086

ogy described in ref. 32. To show the structural differences of studied theoretical approaches, Carbó indices<sup>1</sup> were computed for all possible molecular pairs and are listed in Table V. The Carbó index, which can be denoted as  $C_{AB}$ , is defined as

$$C_{AB} = Z_{AB}(Z_{AA}Z_{BB})^{-1/2} \tag{22}$$

and, in the present work, has been scaled to lie within the range 0–100. Although  $C_{AB}$  values dif-

fer in a small amount, the differences are sufficient to obtain information on the optimal theoretical method to study this kind of molecules. The results suggest that the second-order MP (MP2) method is the theoretical approach that presents the best agreement with the available experimental data for the *cis*-DDP complex. This conclusion is in contrast to the major studies performed until now with organoplatinum complexes, which employ DFT methods by default (see, e.g., refs. 33 and 34). However, the present study overemphasizes

TABLE IV. Principal Structural Parameters for Eight Geometries of Molecular Fragment  $PtCl_2N_2$ .

	CUKRAB <sup>a</sup>	CUSRAJ <sup>a</sup>	B3LYP <sup>b</sup>	HF <sup>b</sup>	MP2 <sup>b</sup>	MP3 <sup>b</sup>	MP4(DQ) <sup>b</sup>	MP4(SDQ) <sup>b</sup>
$R_{Pt-Cl}$	2.32–2.31	2.29–2.28	2.410	2.415	2.406	2.411	2.411	2.414
$R_{Pt-N}$	2.00–2.08	2.00–2.04	2.110	2.126	2.123	2.128	2.129	2.132
$R_{N-H}$	—	—	1.023 1.033	1.005 1.010	1.027 1.034	1.025 1.031	1.027 1.033	1.027 1.033
CIPtCl	92.40	93.21	96.784	97.127	95.880	96.234	96.180	96.042
CIPtN	89.93	88.31–87.09	81.962	83.561	83.290	83.322	83.350	83.289
NPtN	90.94	91.44	99.289	95.751	97.539	97.122	97.120	97.379

<sup>a</sup>Crystallographic structures obtained from CSD.<sup>29</sup>  
<sup>b</sup>Optimized geometries using the Gaussian 94 program.<sup>30</sup>



**TABLE V.**  
**Carbó Index Values for Molecular Fragment PtCl<sub>2</sub>N<sub>2</sub> Used to Compare Different Optimization Methodologies.**

	CUKRAB	CUSRAJ	B3LYP	HF	MP2	MP3	MP4(DQ)	MP4(SDQ)
CUKRAB	100	99.569	98.804	98.800	98.834	98.820	98.821	98.818
CUSRAJ	99.569	100	98.782	98.772	98.806	98.793	98.794	98.791
B3LYP	98.804	98.782	100	99.925	99.762	99.897	99.880	99.826
HF	98.800	98.772	99.925	100	99.601	99.773	99.750	99.700
MP2	98.834	98.806	99.762	99.601	100	99.941	99.954	99.943
MP3	98.820	98.793	99.897	99.773	99.941	100	99.999	99.981
MP4(DQ)	98.821	98.794	99.880	99.750	99.954	99.999	100	99.985
MP4(SDQ)	98.818	98.791	99.826	99.700	99.943	99.981	99.985	100

molecular geometry, and this can explain such comparative results. Another interesting conclusion is that the different levels of MP approach give similar results without appreciable differences between them. The addition of third- and fourth-order perturbations does not give significant changes in the 3-D structure with respect to MP2, but computational requirements increase considerably. In particular, HF appears to be comparable to B3LYP. In accordance with this result, it is possible to assert that the HF method may be useful for the geometrical study of these kinds of organoplatinum complexes.

## Conclusions

The present study corroborates the usefulness of an EJР technique for obtaining first-order ASA density functions. Some algorithm improvements related to the calculation of the EJР rotation angle using a Taylor series expansion are given. In addition, a new set of atomic ASA  $\rho(r)$  is presented for atoms H to Rn. A sound application example is presented relating to QSM and concerning the determination of the best theoretical approach for the geometry optimization of the *cis*-DDP complex.

## Acknowledgments

This work was carried out using the CЕСSA and CEPBA resources, coordinated by C<sup>4</sup>. The second author thanks Prof. S. Huzinaga for providing detailed information on the *ab initio* basis sets. The authors also thank the referees for their constructive criticism, which improved several aspects of this work.

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